Dependence of inherent selective atomic layer deposition of FeO_x on Pt nanoparticles on the coreactant and temperature

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Dependence of inherent selective atomic layer deposition of FeO_x on Pt nanoparticles on the coreactant and temperature

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ABSTRACT

Selective growth of metal oxides on metal via atomic layer deposition (ALD) has attracted great interest due to their potential applications in the semiconductor industry, as well as energy and environment fields. In this work, the influence of an oxidizing coreactant and the reaction temperature on the selective growth of FeO_x on the facets of Pt nanoparticles and low coordination edge sites are studied via *in situ* Fourier transform infrared spectroscopy (FTIR) and first-principles calculations combined with microkinetic methods. It is found that selective deposition on the low coordination edge sites of Pt nanoparticles is realized when using O₃ as the coreactant at low temperature (150 °C), while the ALD reaction takes place only above 250 °C without selectivity when using O₂ as the coreactant. Based on density functional theory calculations, the edge-selective growth of FeO_x on Pt is attributed to energy barrier differences for ALD reactions taking place at the Pt(111), Pt(100), and edge sites. Moreover, reaction rate analysis indicates that the selectivity of FeO_x ALD on Pt nanoparticles is temperature dependent and that a high temperature suppresses the selectivity between different sites, which is also confirmed by the FTIR results.

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I. INTRODUCTION

Pt-based composite nanoparticles (NPs) have been widely investigated in applications such as catalysis, fuel cells, and combustion.^{1,2} It is known that the performance of NPs is related to its size, and the specific activity typically increases with decreasing size.³ However, a decreased size also leads to a larger surface-free energy, which makes NPs unstable.^{4,5} The encapsulation of NPs with an oxide layer has been developed as an effective method to stabilize the NPs.⁶ Recently, atomic layer deposition (ALD) has been considered for encapsulation of NPs because of its precise control in

thickness at the atomic scale.^{7–13} It is worth noting that for surface modification in catalysis, conformal encapsulation is not desired since a complete coating layer may block the active sites of the NPs and separate it from the reactant.^{14,15} The deposition of a porous protection layer is thought to be a feasible way to achieve the desired activity and stability at the same time.¹⁶ In recent research, special attention has been paid to the growth behavior of the coating layer via ALD on Pt NPs.¹³

ALD processes involve precursor adsorption, dissociation, and nucleation, which all depend on the substrate properties.^{17–20} In recent research, it was found that some metal oxide ALD processes

show selective deposition on specific sites and facets of Pt NPs. Previously, our group utilized the different binding energy of Ce(thd)₄ on Pt NPs to realize facet-selective deposition of CeO_x on Pt(111) facets.⁸ In our recent work, first-principles calculations combined with microkinetic methods were employed to study the edge-selective growth mechanism of 3d-transition metal oxide ALD on Pt nanoparticles using metal cyclopentadienyl precursors [M(Cp)₂, M = Fe, Co, and Ni] and the O₃ coreactant. M(Cp)₂ precursor molecules exhibit robust decomposition on the surface of Pt nanoparticles. The reaction rates on different sites of Pt NPs follow the order of edge >(100) >(111), which indicates that low coordination edge sites were inherently selected to be covered and the (111) facets were covered after the first few ALD cycles.²¹ Besides the metal precursor, the coreactant also has a significant impact on the ALD process. It was found that when TMA and H₂O were utilized to deposit Al₂O₃ at a low temperature, the excessive TMA precursor molecules and the methane by-products were hard to be removed, resulting in an incomplete ALD reaction and voids in the Al₂O₃ layer.²² Subsequently, O₃ with a higher reactivity was used to replace H₂O, which enables a more complete consumption of TMA ligands.²³ Furthermore, the reaction temperature also influences the ALD selectivity since it can determine whether a surface reaction occurs or not. The difference of the growth rate on different sites is a key factor that influences the selectivity. Therefore, it is important to investigate the dependence of the growth behavior on the coreactant and temperature during the ALD process for the applications of selective ALD.

In this paper, *in situ* Fourier transform infrared spectroscopy (FTIR) and theoretical calculations were employed to study the influence of the coreactants O₂ or O₃ on the selective deposition of FeO_x on Pt NPs using *tert*-butyl ferrocene (TBF) as the precursor. When TBF and O₂ were used, it was found that the ALD process occurred only above 250 °C, indicating that the organic ligands of the TBF precursor cannot be eliminated by O₂ below this temperature. However, by utilizing O₃ instead of O₂, the edge site was preferentially covered at 150 °C while exposing Pt(111) and Pt(100) facets. Furthermore, it was found that the selective deposition on edge sites was greatly suppressed at a higher temperature (200 °C) when using TBF and O₃. Density functional theory (DFT) calculations show that the decomposition rate differences of the TBF precursor on the Pt (100) facets and edge sites become smaller when increasing temperature, which explains the suppressed edge-selective growth at a higher temperature.

II. EXPERIMENT

A. Sample preparation

The Pt nanoparticles were first deposited on an Al₂O₃ powder substrate by ALD. The Al₂O₃ spherical supports (NANODUR, 99.5%) with an average size of 40 nm and a specific surface area of 32–40 m²/g were purchased from Alfa Aesar, which were usually used as supports for the design and preparation of model catalysts. The role of oxide support is to obtain uniformly dispersed Pt nanoparticles because the interactions between the deposited metal atoms are stronger than those between the metal atoms and the oxide substrate.²⁴ The Pt ALD processes were performed in a custom-made fluidized bed reactor (AngstromBlock Scale-F015 ALD system). The

base pressure for the fluidized bed ALD reactor during Pt ALD was ~1.2 Torr. A total of 200 mg Al₂O₃ powder was weighted and loaded in the powder holder. The Pt ALD process was carried out at 150 °C using trimethyl(methylcyclopentadienyl)platinum (MeCpPtMe₃, 98%, Sigma-Aldrich) as the precursor and O₃ as the coreactant. The Pt precursor was held in a stainless-steel bottle kept at 65 °C during Pt ALD. The pulse time and purge time for the MeCpPtMe₃ precursor were both 200 s. O₃ was introduced to the reactor with the pulse time and purge time of 200 and 200 s, respectively. Two cycles of Pt ALD were performed on all samples, and it is denoted as Pt/Al₂O₃.

B. Sample characterization

The *in situ* FTIR measurements were taken in a specially designed ALD reactor integrated with an FTIR spectrometer, as described in previous studies.^{25,26} The ALD reactor was pumped down to ~10⁻⁶ Torr using a combination of a turbo-molecular pump and a roughing pump. The powder samples were pressed into a tungsten mesh and the IR measurements were carried out in transmission mode. The IR beam source and the detector were separated from the chamber using KBr windows and gate valves. The precursors were dosed into the chamber using ALD valves. In order to prevent the condensation of ALD precursors, the walls of the reactor were heated to 100 °C. For the CO adsorption experiments, the Pt/Al₂O₃ sample with different Fe₂O₃ ALD cycles was transferred to the *in situ* diffuse-reflectance infrared Fourier transform spectroscopy chamber. They were first pretreated at 300 °C (from room temperature, 10 °C/min) by 50 SCCM of O₂ for 30 min to remove possible organic species in the ALD process. Then, the temperature was cooled down to 30 °C. The background spectra were collected in a flow of 50 SCCM of N₂ at 30 °C. CO adsorption spectra were collected after treatment by 50 SCCM of 1% CO. After the spectra are stable, a flow of 50 SCCM of N₂ was used to remove physically adsorbed CO, and the CO chemical adsorption spectra could be obtained.

C. Computational model and method

The pristine surface of nanoparticles consists of different facets, where Pt atoms in these facets and edges are differently coordinated. Here, we considered the low-index facets (100) and (111) to mimic the regular surface of Pt nanoparticles, whereas the joint atomic chains of (100) and (111) facets were constructed to mimic the edge sites of nanoparticles. The 4 × 4 supercells with five atomic layers were used to simulate the TBF adsorption and decomposition on the Pt(111) and (100) slabs, whereas a 13.75 × 14.04 Å² rectangular unit cell with eight atomic layers was used to model the growth of FeO_x on the edge slab. The top three layers of Pt atoms were allowed to relax during the calculations. To eliminate the interaction between the Pt slab and its periodic images, we created a vacuum distance larger than 17 Å for the supercell geometry. The calculations were performed by using the first-principles plane-wave pseudopotential formulation as implemented in the Vienna *Ab-initio* Simulation Package.²⁷ The exchange-correlation functional is in the form of Perdew–Burke–Ernzerh with the generalized gradient approximation. The cutoff energy of 400 eV for the plane-wave basis and a k-mesh of 3 × 3 × 1 were applied for the three Pt slabs [(111), (100), and edge] to ensure the energy convergence to 1 meV, and the residual

force acting on each atom is less than 0.05 eV/Å. The decomposition of the TBF precursor on the Pt surface occurred through two main ways: slipping path and splitting path according to the adsorption orientation.²⁸ Therefore, no ligands were cleaved upon adsorption. The another dehydrogenation path has not been considered in this work due to the higher energy barrier compared with the slipping and splitting paths (Fig. S1^{35,21}).

III. RESULTS AND DISCUSSION

In our previous studies, it was found that when employing $M(\text{Cp})_2$ and O_3 , MO_x ALD showed an edge-selective growth ($M = \text{Fe}$, Co , and Ni) on Pt NPs.²¹ When changing the metal element in the precursor, the preferential deposition on edge sites still occurs.¹³ Herein, TBF and O_2 are used as the metal precursor and coreactant, respectively, to investigate the selective deposition of FeO_x on Pt NPs. *In situ* FTIR spectra are measured to study the ALD process and to detect CO adsorption on Pt after FeO_x deposition. Initially, the FeO_x ALD process is studied by *in situ* FTIR measurements after TBF and O_2 doses at 300 °C. As shown in Fig. 1(a), following the TBF dose, the main vibration peak of TBF ligands on Pt is located at about 1100–1700 cm^{-1} , which can be assigned to the C=C bond and C-Fe bond of the TBF precursor.^{29–32} This spectrum illustrates that the TBF precursor can adsorb on the Pt surface during the ALD process. However, the C-H stretching vibration peaks of ligands belonging to the TBF precursor at 2700–3000 cm^{-1} are not detected, which may be due to dehydrogenation reactions on the Pt NPs.^{33,34} After an O_2 dose of 200 s, the peak intensity decreases, meaning that the ligands are eliminated by O_2 at 300 °C. Nevertheless, the intensity of the TBF ligands still remains at 1100–1700 cm^{-1} , which suggests that 200 s O_2 dosing time is not enough to remove all organic ligands.³⁴ In contrast, after 15 min O_2 dosing, the characteristic vibration peak for the TBF precursor ligands almost disappears, which indicates that the O_2 dose can eventually eliminate most of the residual organic

ligands. Accordingly, in the rest of the FeO_x ALD experiments, 15 min of O_2 pulse is used.

Figure 1(b) shows the *in situ* CO adsorption spectra after different numbers of FeO_x ALD cycles on Pt. The intensity of the CO adsorption peak decreases with increasing FeO_x cycles, which indicates that the Pt surface becomes covered by FeO_x . The linear adsorption peak can be divided into three peaks, which can be assigned to CO adsorbed on the Pt(111) and Pt(100) facets and on Pt's low coordinated sites such as edges and corners.²⁷ Here, it is assumed that the low-coordinated sites are the edges, because the vertex sites only occupy a small part of the surface area of the nanoparticle. The percentage of peak area for the remaining Pt sites exposed for CO adsorption is calculated, as plotted in Fig. 1(c). After 1 cycle FeO_x ALD, the percentage of the signal corresponding to the edge sites decreases significantly from 100% to 59% and the (100) facet also shows a little decrease compared with the pristine (100) facet, while the intensity assigned to the (111) facet stays the same [Figs. 1(b) and 1(c)]. These results show that the Pt(111) facet is more inert than the other sites during the first cycle and that the Pt(100) and edge sites are coated first. After performing eight ALD cycles, the CO absorption intensity of the three different types of sites decreases and mainly the (111) facet remains exposed. The drastically decreased intensity of (100) and edge sites suggests that the selective growth on edge sites is poor when using TBF and O_2 at 300 °C.

Subsequently, the selective growth of FeO_x at a lower temperature using O_2 as the coreactant is investigated. As shown in Fig. 2(a), a similar vibration peak of TBF ligands at 1100–1700 cm^{-1} is observed after the TBF dose, which indicates the absorption of the TBF precursor on the Pt surface at 150 °C. However, following the O_2 dose, the difference spectrum is flat (with the saturated TBF adsorption spectrum as the reference), which suggests that the half reaction of the O_2 dose is not completed at this condition. At 200 °C, the results are similar as shown in Fig. 2. Only TBF adsorption occurs, which suggests that 200 °C is still not in the ALD temperature window. At 250 °C, the difference spectrum shows a

FIG. 1. (a) *In situ* FTIR spectrum during the FeO_x ALD process on Pt NPs using TBF and O_2 at 300 °C using the spectrum before TBF dose as the reference. (b) CO adsorption spectra on FeO_x -coated Pt nanoparticles with different ALD cycles using TBF and O_2 at 300 °C. (c) Three divided peak percentages of Pt (111), (100) facets, and edge sites of Pt NPs with different FeO_x coating cycles using TBF and O_2 at 300 °C.

FIG. 2. *In situ* FTIR spectra of the FeO_x ALD process on Pt NPs using TBF and O₂ at different temperatures using the previous dose as the reference spectrum (1 TBF represents 1 dose TBF precursor) (a) 150, (b) 200, and (c) 250 °C. (d) CO adsorption spectra on FeO_x-coated Pt nanoparticles with different ALD cycles using TBF and O₂ at 250 °C.

negative peak, which demonstrates that the residual ligands of the TBF precursor are consumed and the second half-reaction occurs. To summarize, this series of *in situ* FTIR measurements shows that the adsorption of the TBF precursor during ALD can take place at 150 °C and at a higher temperature, but the second half-reaction can be completed only at temperatures of 250 °C and higher when using O₂ as the coreactant.

When the ALD process with O₂ is carried out at 250 °C, the selectivity of the edge sites cannot be observed [Fig. 2(d)]. Therefore, it is clear that O₂ can eliminate the ligands belonging to the TBF precursor only above 250 °C, which indicates that the elimination of the precursor ligands may also influence the whole reaction rate and selectivity. When a high temperature is used, the rate difference of adsorption and decomposition between different sites may decrease and result in decreased selectivity, as shown in Fig. 2(d).

The whole ALD reaction can be completed only at a high deposition temperature (250 °C) when using O₂ as the coreactant, while the selective deposition on the specific sites of Pt NPs is poor. Therefore, the more reactive coreactant O₃ is used instead of O₂ during the ALD process, which means ALD can be performed at lower substrate temperatures. This extended temperature window enables the study of the impact of temperature on the selective

deposition. When using TBF and O₃ at 150 °C, the growth of FeO_x is confirmed by x-ray photoelectron spectroscopy (XPS) [Fig. 3(a)]. The FeO_x deposition does not lead to a significant change of the average size of the Pt NPs [Figs. 3(b) and 3(c)]. Figure 4 shows the fitting curves of linear CO adsorption spectra on FeO_x-coated Pt nanoparticles using TBF and O₃ at different temperatures. It is found that after the first FeO_x ALD cycle at 150 °C, the FTIR signal of edge sites immediately decreases compared with the pristine sample, while the intensity of other sites remains constant, which reveals that the FeO_x first initiates on the edge sites of Pt [Figs. 4(a) and 4(b)]. These results indicate that for this condition, FeO_x is preferentially deposited on the edge sites. When increasing ALD cycles, the intensity assigned to the (100) facet also begins to decrease, suggesting the growth of FeO_x on the Pt(100) facet. These results indicate that in this situation, the deposition rate of FeO_x on Pt follows the order of edge sites >(100) >(111) (Fig. S2³⁵). Subsequently, high-temperature ALD growth of FeO_x is employed to investigate the temperature effect on the selective growth on these facets and edge sites. Figures 4(c) and 4(d) show the FTIR peaks of CO adsorption for 1 cycle of FeO_x-coated samples at 200 and 300 °C, respectively. In contrast to the data for 150 °C [Fig. 4(b)], it is found that the signal of (100) decreases significantly along with

FIG. 3. (a) X-ray photoelectron spectroscopy (XPS) element scans for the Fe 2p of Pt nanoparticles with and without FeO_x coating (1 cycle, TBF + O₃, 150 °C). Transmission electron microscopy image of (b) pristine Pt nanoparticles and (c) Pt nanoparticles with 1 cycle FeO_x coating.

FIG. 4. Fitting curves of linear CO adsorption spectra on FeO_x-coated Pt nanoparticles with different ALD cycles using TBF and O₃: (a) 0 cycles, (b) 1 cycle at 150 °C, (c) 1 cycle at 200 °C, and (d) 1 cycle at 300 °C.

FIG. 5. (a) Minimum energy path of TBF decomposition on Pt (100), (111) facets, and edge sites. The calculated decomposition rates of the TBF precursor on Pt (100), (111) facets, and edge sites (b) at 150 °C and (c) from 150 to 300 °C.

the decrease of the peak associated with edge sites. This implies that an almost simultaneous growth of FeO_x on (100) facets and edge sites occurs, suggesting that the edge selectivity is suppressed at a higher temperature. Besides, the lower CO absorption intensity at a higher temperature indicates the increased growth rate of FeO_x when increasing the temperature.

DFT calculations and the microkinetics method are performed to clarify the difference of the FeO_x growth on Pt (100) and (111) facets, and edge sites. The subsequent decomposition paths of the TBF precursor on different facets or edge sites are plotted in Fig. 5(a). It is found that the dissociation energy barrier of TBF on Pt surfaces follows the order of the (111) > (100) > edge, which suggests that the TBF precursor would preferentially dissociate on the Pt edge sites. The decomposition rates of the TBF precursor on different Pt facets at 150 °C are also calculated, as shown in Fig. 5(b). The results show that the decomposition rates of the TBF precursor on the edge sites are much higher than those on the (100) facets, which is responsible for the edge-selective growth of FeO_x in experiments. Moreover, the impact of temperature on the decomposition rates of the TBF precursor on Pt different facets is also calculated, as depicted in Fig. 5(c). When increasing the temperature, the difference between decomposition rates on Pt(100) and edge sites decreases (10⁹ at 150 °C to 10⁷ at 300 °C), which explains the suppressed edge-selective growth at a higher temperature. Our calculations indicate that the temperature plays an important role in the selectivity of ALD growth.

IV. SUMMARY AND CONCLUSIONS

The edge selective behavior of FeO_x on Pt NPs using the TBF precursor is studied by the *in situ* FTIR method combined with DFT calculations. The *in situ* FTIR measurements show that the adsorption of TBF on a Pt surface can occur at low temperatures, while the O₂ half-reaction can be completed only above 250 °C. At such a high temperature, the growth rate difference of FeO_x on a different site of Pt becomes smaller, which leads to the simultaneous growth on Pt (100) facets and edge sites. On the other hand, when O₃ is used, the oxidation reaction can occur at low temperature (150 °C) and edge-selective growth of FeO_x on Pt is achieved. Our work shows that both the coreactant and deposition temperature

have a large influence on the selectivity of metal oxides on metal nanoparticles, which sheds light on the precise design of novel metal-oxide composite structures with unique properties.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material.

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